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CORROSION CONTROL IN THE BLEACH PLANT

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ABSTRACT

Although the conditions existing in the chemical bleach plant can be extremely corrosive, effective methods are available to minimize corrosion damage. These methods include specification of titanium or high molybdenum stainless alloys, use of glass fiber-reinforced polymerics as linings and monolithic vessels, use of electrochemical protection, and modification of environments with antichlor compounds. Selection of a corrosion control strategy depends on the costs of different options and the severity of corrosion in the mill.

INTRODUCTION

Few aspects of pulp and paper production are as corrosive as the typical bleach plant. The strong oxidants and acidic environments which are effective in bleaching processes are equally effective in attacking the common structural materials. Corrosion control methods must be used in the preparation, handling, and storage of the bleaching liquors or severe corrosion will result. Pitting and crevice corrosion are particularly severe problems in many of the bleaching stages, and steps must be taken to minimize these forms of corrosion for economical operation of the bleach plant. Even atmospheric corrosion of the building and structures in the bleach plant offers unique challenges to corrosion-free operation.

The high cost of corrosion of bleaching equipment was demonstrated by Mueller and Davy (1) in their study of corrosion costs in pulp and paper production. In 1974, the additional costs due to corrosion — costs associated with capital equipment expenditures for exotic alloys and for maintenance and repair, but excluding lost production costs — were estimated at \$1.75 per ton of production. In a bleached kraft mill, the cost of corrosion in the bleach plant was estimated at 25 percent of the total corrosion costs. If the \$1.75 is adjusted for inflation between 1974 and 1986, the costs per ton associated with corrosion control in the bleach plant may be as high as \$4.50 per ton.

Fortunately, considerable progress has been made in reducing corrosion costs in the bleach plant. Many options are available to mills seeking to minimize the cost and aggravation of corrosion damage. Alloys are available whose corrosion resistance and cost can be matched to the corrosiveness of the environment, ranging from type 316L stainless steel to titanium (Table 1). The use of nonmetals in the bleach plant has expanded tremendously, offering a low cost alternative to stainless alloys in many applications. Even electrochemical protection methods, which might

have been considered exotic a decade ago, have been embraced by the industry in an effort to control overall costs. Different approaches are used in different applications, depending on the severity of the corrosion problem and the mill strategy for controlling maintenance and repair costs.

Table 1 Typical compositions of some corrosion-resistant alloys (4)

Alloy	C	Cr	Ni	Mo	Cu	Fe	Ti	N	Other
316L	0.016	17	11	2.1	—	Bal	—	—	—
317L	0.012	19	15	3.6	—	Bal	—	—	—
254SMO	0.011	20	18	6.1	0.7	Bal	—	0.20	—
Al-6X	0.028	20	25	6.1	—	Bal	—	0.06	—
904L	0.024	20	24	4.4	4.1	Bal	—	0.06	—
C-276	0.004	15	55	15.8	0.1	5.8	—	—	3.7W, 2Co
Ti Gr. 2	0.02	—	—	—	—	0.03	Bal	0.02	—
Ti Gr. 12	0.08	—	0.1	0.3	—	0.03	Bal	0.03	0.15 O2
Trademark	Product of...								
Al-6X	Allegheny Ludlum Steel Co.								
254 SMO	Avesta Jernverks AB.								
904L	Uddeholm Corp.								
C-276	Cabot Corp.								

A variety of different corrosion problems can be encountered in a bleach plant, depending on the type of bleaching stages in use. Corrosion concerns are quite different for peroxide bleaching compared to chlorine bleaching because of the different environments encountered in each different process. Greater detail is available in references (2-3).

FORMS OF CORROSION IN THE BLEACH PLANT

Many different types of corrosion damage are encountered in the typical bleach plant, including pitting, crevice corrosion, stress corrosion cracking, and general attack. At present, the most worrisome forms of corrosion are pitting and crevice corrosion that occur on stainless steel equipment in C, D, C/D, and H stages. However, there is the potential for other forms of corrosion damage, such as the rapid attack that occurs on titanium if it is inadvertently exposed to dry chlorine gas. Stress corrosion cracking can also occur, in caustic storage tanks if the concentration or temperature exceeds certain limits, or in the acid chloride environments associated with washer filtrates.

Metals resist corrosion damage for one of two reasons. Precious metals, such as gold and platinum, are thermodynamically immune to corrosion in most aqueous environments, but these metals are prohibitively costly for most structural applications. Most structural alloys resist corrosion

because they spontaneously form a tight, adherent, impervious surface film that protects the underlying metal from contact with the corrosive electrolyte. The film is called a passive film because it passivates and prevents corrosion of metals which are thermodynamically very reactive. In stainless steels, for example, the protective film is a very thin layer rich in chromium and oxygen. With titanium, the film is a thin layer of TiO_2 that isolates the alloy substrate from attack. All of the alloys commonly used in the bleach plant rely on passive films for corrosion resistance. As long as these passive films are intact, corrosion rates will remain very low.

Localized Corrosion Processes

Pitting. Pitting is the localized corrosion that occurs when the passive film on a metal surface is attacked at isolated sites and is unable to restore itself. Events occur as shown in Fig. 1, leading to rapid penetration of pits into the metal surface. Wherever the film is damaged, the underlying metal experiences rapid corrosion. The rest of the surface is protected by the passive film and remains a cathode. A differential corrosion cell between the localized anode and the extensive cathode surface is established.

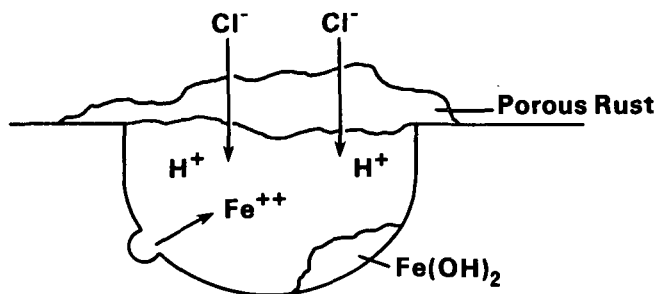
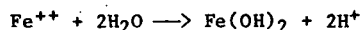


Fig. 1 Schematic diagram showing processes which produce HCl in pits.

This differential cell promotes preferential corrosion at the anode, leading to the presence of isolated "holes" in an otherwise passive metal surface. Pitting is particularly frustrating, in that most of the metal surface remains intact and apparently free of corrosion, while the function of the item is compromised by pit-induced perforations.

The preferential corrosion occurring at an anode induces two changes in the electrolyte which greatly accelerate the rate of attack. First, the rapid dissolution of metal ions into this localized electrolyte results in precipitation of metal ion hydroxides, e.g.,



This precipitation scavenges hydroxide ions from the electrolyte near the anode, generating a local environment which is generally much more acidic than the bulk electrolyte. In fact, pH values of 1 or lower have been measured in the electrolyte trapped in a pit. The second change in

the pit electrolyte is enrichment in aggressive anions (e.g., Cl^-) in order to balance the positive charge introduced by metal ion dissolution. As a result of these two processes, the environment trapped in an active pit resembles a concentrated hydrochloric acid solution, even if the bulk environment appears innocuous. Reestablishing a protective surface film in the presence of such a concentrated acid is difficult, and the pitting process usually continues once initiated.

Pitting occurs only on passive metals such as stainless steels. The passive film must be present to concentrate the attack at a few sites where the film is susceptible to damage. A metal undergoing uniform corrosion without forming a surface film will not pit by the classical mechanism, although local variations in corrosion rate are sometimes seen.

Susceptibility to pitting is greater in environments containing strong oxidants, low pH values, and high concentrations of aggressive anions such as Cl^- and S^{--} . Strong oxidants such as dissolved chlorine initiate pitting corrosion by attacking weak sites in the protective film. Consequently, pitting is strongly dependent on the amount of oxidant present in the corrosive solution. Aggressive anions and acidic solutions promote attack at weak sites in the protective film, and pitting susceptibility increases with increasing concentration of chloride, sulfide, and other aggressive anions. Susceptibility is also increased with increasing temperature.

Pitting susceptibility is also affected by the electrochemical potential (i.e., voltage) which exists at the metal surface. A potential develops spontaneously whenever a metal is in contact with an electrolyte. The spontaneous potential assumed by a metal is labelled its corrosion potential, E_{corr} .

The sign and magnitude of the corrosion potential depend on the composition and structure of the metal and the composition of the electrolyte. In particular, the potential is affected by the presence of oxidizing species in the solution, such as chlorine and chlorine dioxide, both of which raise the potential in proportion to their concentration.

When E_{corr} for a metal rises above a threshold potential known as the pitting potential, E_p , pitting occurs immediately and may continue even if the corrosion potential is subsequently lowered.

To minimize the likelihood of pitting in service, it is desirable that E_p be at least several hundred millivolts above the typical E_{corr} potential. Then, during brief excursions in the concentration of chlorine or some other oxidant, the momentary surge in corrosion potential does not exceed the threshold for the onset of pitting.

Crevice Corrosion. Crevice corrosion is metal dissolution that occurs wherever part of a nominally passive metal surface is isolated from intimate contact with a surrounding electrolyte. Isolation may occur because improper design or construction introduces crevices, or because of the formation of scale, deposits, or fiber masses.

Crevise corrosion shares many similarities with the pitting process, but the origins are somewhat different. In crevice corrosion, the restricted area (e.g., underneath a deposit) becomes an anode because oxidants present in the bulk electrolyte are excluded from these areas. Most of the surface is bathed in oxidizing species and becomes cathodic. This promotes corrosion of those small areas with restricted access to the bulk electrolyte. Once initiated, the mechanism of propagation of crevice corrosion involves the development of acidic electrolytes which are enriched in aggressive anions like Cl^- .

Susceptibility to crevice corrosion also depends on the composition, temperature, and pH of the environment in a fashion similar to pitting. The deleterious effects of oxidizing species will be particularly evident in crevice corrosion, since it is the difference in oxidizing power underneath deposits that concentrates the attack within the crevice. Although the dependence of crevice corrosion on potential is similar to that described above for pitting, there is no corresponding threshold potential for crevice corrosion; such potentials will depend on the geometry and characteristics of the crevices which are present.

Stress Corrosion Cracking

Stress corrosion cracking occurs when a metal is subjected to a tensile stress while exposed to an environment that promotes crack initiation and growth. Tensile stresses can occur as a result of process conditions — hoop stresses in pressure vessels, for example. Stresses can also remain within the metal as a consequence of manufacturing or fabrication processes — the residual stress in the vicinity of a weldment is an example.

Usually, stress corrosion cracking of a family of alloys will only occur in specific environments. Copper alloys will crack in ammoniacal solutions but not chlorides, whereas the opposite is true for stainless steels. In bleaching applications, stress corrosion cracking is usually a concern only for plain carbon steel exposed to concentrated hot caustic environments, and for some stainless steels exposed to bleach plant filtrates containing high levels of chlorides at elevated temperatures.

Uniform Corrosion

Uniform or general corrosion, which results in a uniform wastage of the metal surface, is rarely seen in bleach plant equipment because of the corrosion-resistant materials used in these applications. Equipment fabricated from plain carbon steel or other materials susceptible to uniform corrosion would disappear soon after exposure to bleaching environments. Nonetheless, uniform corrosion is occasionally encountered. For example, rapid uniform corrosion can occur when titanium is exposed to dry chlorine gas. In chlorine, the protective oxide film cannot form and the titanium is rapidly converted to titanium chloride, accompanied by considerable heat and green fire.

CORROSION CONTROL IN BLEACHING STAGES

The greatest corrosion concern in the bleach plant is associated with the bleaching stages themselves, especially those involving chlorine compounds. Severe attack can occur on stainless steel equipment in conventional C and D stage bleaching, including such components as washer drums, showers, etc. The characteristics of localized corrosion are similar in chlorine and chlorine dioxide stages of the bleaching process, although the D-stage is generally acknowledged to be somewhat more corrosive because of its higher temperature.

The environments are equally aggressive in other parts of the bleach plant, but the unique design of washing equipment prevents the use of acid brick and other resistant materials of construction which minimize corrosion. In displacement bleaching, the environments are perhaps more severe than in conventional bleaching, but the corrosion concerns are allayed with all-titanium construction.

Considerable progress has been made in identifying methods for controlling the high cost of corrosion in the various bleaching stages. These methods include selection of alloys with improved corrosion resistance, selection of nonmetals for use as coatings or in monolithic construction, utilization of electrochemical protection, and control of residual oxidants in various washing processes. Many of these methods have been used in combination — e.g., use of type 317L stainless steel in conjunction with electrochemical protection. Since many of these methods have been successful in combatting corrosion, a mill may choose a corrosion control option based on economics and their overall corrosion control strategy. No consensus has yet appeared regarding the optimal method of controlling corrosion costs in the bleach plant.

Environmental Conditions

Closure. Bleach plant closure to reduce effluents has generally exacerbated corrosion concerns throughout the bleach plant. For C and D stages, closure results in an increase in the temperature, chlorine or chlorine dioxide residual, and total organic loading. In general, a decrease in the pH occurs with closure, particularly in the C-stage washer sections. Each of these changes in filtrate character is thought to increase the severity of localized corrosion of stainless steels used in bleach plants.

Closure has also affected other circumstances in the bleach plant. For example, the use of some nonmetallic materials such as rubber linings is restricted because of the carryover of ClO_2 which attacks many rubber compounds. It is also necessary to avoid the use of D stage filtrates in C-stage showers, since the low pH will regenerate chlorine dioxide from the relatively innocuous chlorites present in D-stage filtrates.

Chlorination Stage. Corrosion of metallic materials in chlorination bleaching is affected by

the composition of the filtrate (residual Cl_2 , chloride), pH, and temperature. Considerable variation in these quantities is evident from mill to mill, depending on the processes used.

In the typical bleaching stage, (1) pulp is diluted to low consistency, (2) intimately mixed with chlorine, (3) held in a retention tower for reaction, and (4) washed in a rotary filter washer. The same process may be accomplished in different stages of a displacement bleaching system, in which case a pulp mass is constrained to move vertically in a vessel while bleaching liquors are recirculated through the pulp.

During the bleaching process, the chlorine gas reacts with lignin and forms HCl as a product of the reaction. Depending on the residual alkalinity of the incoming pulp, the hydrochloric acid generated will lower the pH of the C-stage pulp slurry in the range, 0.5 to 3. These highly acidic conditions are challenging for most materials of construction.

In the past, temperatures in the chlorination stage were kept relatively low, on the order of 25 to 40 C, because of the rapidity of the chlorine reaction and the corresponding opportunities for pulp degradation. In recent years, high temperature chlorination stages have appeared as a result of closure and recent improvements in control of the chlorination process. Chlorination may occur at temperatures ranging from 40 to 60 C, and these higher temperatures affect corrosion resistance. In particular, the upper temperature limits for widely used polymers is being approached in closed mills.

The chloride concentration in corrosion washer filtrate will increase in proportion to the amount of chlorine reacted. The range varies approximately from 500 to 5000 ppm, depending on closure.

The residual chlorine in the washer filtrate will range from 0 to several hundred parts per million, depending on the bleaching conditions. Very low chlorine residuals are seen following high temperature chlorination because of the rapid reaction rates. Very low chlorine residuals can also be achieved in the pulp entering the washer with the use of SO_2 as an antichlor.

Chlorine Dioxide Stage. Rapson (this volume) has summarized the optimum conditions for D-stage bleaching as follows:

ClO_2	0.6 to 1.0% on pulp
Consistency	11-12%
Retention time	3 hours
Temperature	70 C
Terminal pH	3.5-4.0

The characteristics of the D-stage filtrate were summarized for eight mills examined in an on-site corrosion study sponsored by TAPPI (4). The pH ranged from 2.1 to 7.7, with an average value for the eight mills of 4.9. Temperatures ranged from 53 to 80 C. ClO_2 residuals ranged from 0 to 180 ppm and chlorides ranged from 500 ppm to 5600 ppm.

Materials of Construction

Although there is great potential for severe attack throughout all stages of the traditional bleaching processes, most of these problems have been resolved through judicious selection of materials of construction. The use of highly alloyed stainless steel, titanium, and FRP has been successful in eliminating many of the most worrisome corrosion problems. Other methods have also been applied with success, including electrochemical protection and improved control of process chemistry.

Largely through trial and error, suitable materials of construction have been identified for use in the various bleaching stages. Laliberte (5) compiled a comprehensive list of bleach plant materials more than a decade ago. This list, with additions and amendments, is included in Table 2.

Table 2 Materials of construction for bleach plant service

Equipment	Stage	Materials
Stock line before chemical addition	C,E,H,P	316L, 317L, FRP
	D	as above, Ti, 4.5 Mo
Stock line after chemical addition	C,D	317L, 4.5 Mo, C-276, Ti, FRP
	E,H,P	316L, 317L,
Mixer 6 Mo, C-276	C	Rubber-lined steel, Ti, FRP,
	D	Ti, FRP, 6 Mo, C-276
	E,H,P	316L, 317L
Bottom agitators and tower mixers	C,D	Ti, C-276, 317L, 6 Mo
	E,H,P	316L, 317L
Stock line from rubber-lined tower	C	317L, Ti, FRP, 6 Mo, C-276, steel
	D	Ti, FRP, 317L, 6 Mo, C-276
	E,H,P	316L, 317L
Washer vat ceramic tile on reinforced concrete	C	Rubber-lined steel, 317L, 6 Mo, FRP, with polyester mortar and polyester membrane
	D	As above, no rubber
	H	Tile over reinforced concrete, portland cement joints, no polyester FRP
	E	Tile over reinforced concrete, portland cement joints
Shower pipes	C,E,D,H	316L, 317L, 4.5 Mo, 6 Mo, Ti, FRP
Drum	C	316L, 317L, 4.5 Mo, 6 Mo, Ti, FRP, FRP lining, rubber-lined steel
	D	317L, 6 Mo, Ti, FRP, FRP-lined steel
	E,H	316L, 317L
Hood	C,E,H,D	FRP, 316L, 317L, Ti
Filtrate piping	C,D	FRP, 6Mo, Ti
	H,E	316L, 317L,
Seal tank mortar, FRP	C,D	Tile lined with polyester resin
	E,H	Tile lined with portland cement mortar, FRP

In the most severe environments such as retention towers, extensive use is made of nonmetal linings. Rubber linings over plain carbon steel are used widely for chlorination service (never for chlorine dioxide service), and extensive use is made of ceramic tile or acid-resistant brickwork, both placed over a suitable polymeric membrane and grouted with polyester mortar.

Extensive use is also made of the molybdenum-bearing stainless steels and other exotic alloys. Types 316L and 317L stainless steels containing two to three and one-half percent molybdenum are widely used, and proprietary alloys containing as much as 6% molybdenum are beginning to emerge as a compromise choice with acceptable corrosion resistance and moderate cost. In smaller equipment, and in very demanding applications such as dynamic and static mixers and C and D stage washers, more expensive alloys such as titanium and Hastelloy C may be specified.

Extensive use is made of glass-reinforced polyester and vinyl ester equipment for applications where abrasion and erosion are not a concern. The record of corrosion resistance of FRP in the bleach plant has been generally good, although not unblemished.

In every instance, an effective material of construction has been identified for each application in the bleach plant, but less expensive alternatives continue to be actively sought.

Bleach Plant Washers

Special attention is drawn to bleach plant washers in chlorine, chlorine dioxide, and hypochlorite service because of continuing problems with localized corrosion of stainless steel components in these applications. Pitting and crevice corrosion such as that shown in Fig. 2-3 are commonly seen on stainless steel drums, vats, and shower piping in C and D stage service. Attack in D stage washers appears to be somewhat more severe than in the C stage, apparently as a result of higher average temperatures in D stage filtrates. Extraction stage washers and washers in hypochlorite service are much less susceptible to localized corrosion because of the alkalinity of these filtrates.

Crevice corrosion is a severe problem in C and D stage washers because of the highly oxidizing nature of the environment and the myriad opportunities for crevice formation. Washer drums are replete with crevices as a result of their design. The intersection of the backing wires and grooves are natural crevices, as are the intersections of backing wires and face wires. Scale deposits — such as barium sulfate and calcium oxalate — can also introduce crevices which subsequently promote localized corrosion. The crevices formed beneath fiber deposits can also act to initiate crevice corrosion on stainless steels with inadequate corrosion resistance.

High chlorine or chlorine equivalent residuals in the C or D stage filtrate are sufficient to initiate localized corrosion in all but the most resistant alloys. Hendricksen (6) has shown that as little as 25 ppm (0.025 g/L) active chlorine is

sufficient to initiate crevice corrosion, whereas residuals as high as several hundred parts per million are often found in C and D stage filtrates.



Fig. 2 Localized corrosion of the deck in a type 316 stainless steel washer.

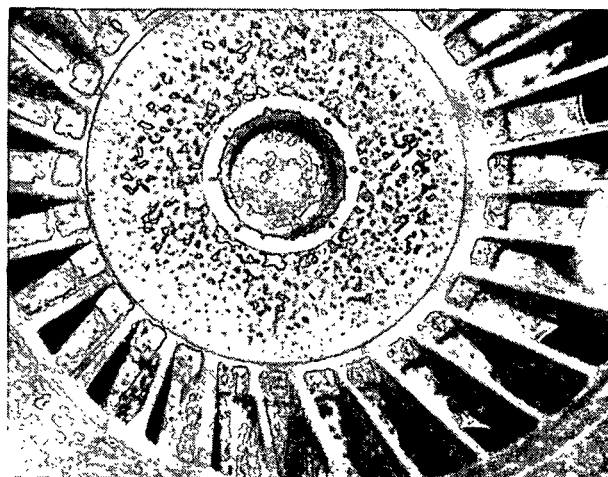


Fig. 3 Localized corrosion of the CF-8M stainless valve in a chlorination stage drum washer.

It appears that the rate of corrosion is more severe in the vapor space above washer drums than in the continuous immersion zones. The TAPPI bleach plant survey (4) and other studies (7-8) clearly revealed higher corrosion rates on stainless steel specimens exposed in the vapor space of C and D stage washers, compared with continuously immersed specimens. The damage is severe because the concentrations of chlorine and chlorine dioxide are increased in the wet films on shower pipes and other surfaces in the vapor space. Severe external corrosion is often seen on stainless steel shower pipes. Even titanium has been defeated by crevice corrosion occurring under fiber deposits on shower pipes in a D stage washer (9).

The severe attack of stainless steels in C and

D stage washers continues to be a concern because of the aggressiveness of the filtrates resulting from closure and other changes in process conditions. As shown in Table 3, temperatures of C-stage filtrates have steadily increased over the past two decades, as bleach plants are closed and freshwater usage is curtailed. Chloride concentrations have also increased and pH levels have fallen — below 1 in some cases. As a result, stainless steels which had once withstood the ravages of corrosion in C and D stage washer service may no longer be adequate.

Table 3 Changes in chlorination stage filtrate conditions with time (14)

Survey	Date	Residual Oxidant	pH	Temp.	Cl-
CPPA	1964	0.11 g/L	2.0	16 C	—
CPPA	1973	0.11	2.0	25	917 ppm
TAPPI	1976	0.09	2.1	33	780
CPAR	1977	0.03	1.8	38	—
PPRIC	1979	0.09	2.0	39	1705

As a result of these changes, Type 317L stainless steel is now considered the minimum alloy for use in bleach plant washer service. Even then, lifetimes of five years or less should be anticipated. Type 316L stainless steel is usually adequate for service in alkaline extraction stages and may be suitable for hypochlorite washers, as well. The alkalinity of these environments mitigates the development of acid in pit electrolytes and forestalls pitting and crevice corrosion.

Acceptance of high corrosion rates in C and D stage washer components is basically an economic decision, since the means to eliminate such corrosion are available. Effective options include the specification of titanium or highly alloyed stainless steels, use of FRP linings on vats, washer drums, and showers, use of electrochemical protection methods, and effective use of antichlor compounds to neutralize the active chlorine residual. An economic decision is usually made whether the costs of these alternative remedies are attractive compared to the cost of periodic replacement of washer drums and associated components.

Titanium in Bleach Plant Washers. In general, titanium has provided excellent resistance to corrosion in both C and D stage washers' service for periods in excess of thirty years. The first all-titanium bleach washer drum, installed in 1955, was untouched by corrosion twenty years later (10). Since 1955, more than 60 titanium washer drums have been installed throughout the world (11), but nearly all are titanium-lined carbon steel rather than monolithic titanium. There have been no reports of significant corrosion of a titanium washer drum, although one report of corrosion induced by improper acid cleaning was at first thought to be caused by chlorine exposure (12).

Titanium has also been used in many other C and D stage washer components, including showers, vats (apparently only in Scandinavia), piping, and hoods. One instance of failure of a titanium shower pipe has been reported (9), but the experience has generally been excellent.

A titanium washer drum is significantly more expensive than a 316L stainless drum. One might expect to incur a premium on the order of 80% for titanium construction.

High Molybdenum Stainless Steels. The resistance of stainless steels to localized corrosion in bleach plant washers is related directly to the molybdenum content of the steel. In recent years, austenitic stainless steels containing 6% molybdenum have shown considerable promise for use in chlorine and chlorine dioxide washer service. The metallurgical structure of 6% molybdenum alloys makes them relatively easy to fabricate into washer components, whereas higher molybdenum alloys are generally unworkable.

Several corrosion coupon surveys have shown that the higher molybdenum content provides a significant improvement in the corrosion resistance of stainless steel, provided care is taken during weld fabrication. Avesta 254 SMO was one of the first 6% Mo stainless steels to be available, but many others have been marketed, including AL-6XN, Cronifer 1925 hMo, and 20 Mo6.

Stainless steels with 4.5% Mo perform significantly better than 317 stainless in drums, but do not match the performance of the 6% alloys. Bardsley (11) found the following lifetimes for stainless steels in chlorination washer service:

Type 317L...1 to 4 years

4.5% Mo Stainless...6.5 to 8 years

The 6% Mo stainless steels had minimal corrosion problems. Garner (14) also suggested that increased molybdenum levels geometrically increased the lifetime of stainless steel washer drums.

A drum washer fabricated from one of the proprietary, high-molybdenum alloys will also be more expensive than a 316L stainless drum; for a 6% alloy, a premium of 30% might be anticipated.

Electrochemical Protection. Crevice corrosion of bleach plant washers and vats can be reduced by imposing a cathodic polarization on the wetted metal components. This polarization is a negative shift in the voltage present at the wetted metal surface — a shift away from the pitting potential of the metal. The voltage shift is achieved by passing a controlled current between the protected structure and an anode which is permanently immersed in the stock at the bottom of the vat. Since the current must flow through the pulp slurry, only wetted surfaces are protected. A schematic diagram of the electrode arrangement is shown in Fig. 4.

The potential of the equipment is typically shifted a few hundred millivolts in the negative direction to protect against crevice corrosion.

In effect, this shift lowers the effective E_{corr} value for the metal, which increases the separation of E_{corr} and the threshold potential for pitting or crevice corrosion. When the potential of the metal is maintained well below the threshold potential for localized corrosion, the likelihood of attack during momentary excursions in residual chlorine is lowered considerably. Special crevice corrosion coupons are usually installed on the protected structure and monitored periodically to ensure that the potential shift is adequate for continued protection.

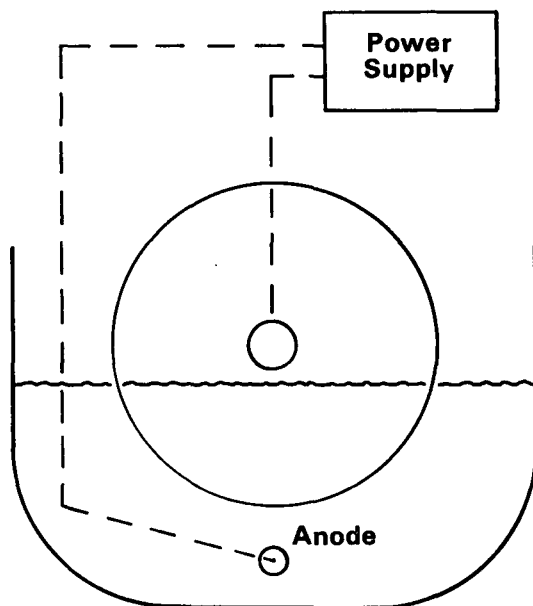


Fig. 4 Schematic diagram of a simple system for electrochemical protection of a washer drum.

Electrochemical protection of bleach plant washer drums is now widely accepted by the industry. The first commercial system was installed in 1977, and now more than 70 systems have been installed in North America. Numerous Scandinavian installations have also been reported. Several stainless steel vats have also been protected, but the simultaneous protection of drums and vats increases the complexity of the installation significantly. In Finland, electrochemical protection has also been used to protect other components in bleach plant service, including a type 317 ball valve at the bottom of a D stage bleaching tower and a type 317L pipe carrying D₂ stage washer filtrate (13).

Extensive evidence shows that electrochemical protection is effective in reducing the rate of attack of stainless steels in bleach plant washer service. Garner recently summarized the status of coupon monitoring on the first six washers protected by electrochemical protection (14). These units were energized during January, 1978 to October, 1981. Included were five D stage washers (2 D₁ and 3 D₂) and one C stage washer. Garner found that even the least effective electrochemical protection system halved the corrosion rate

found on unprotected metal, while the most effective system reduced the corrosion rate by a factor of 12. On average, electrochemical protection reduced the rate of attack of the protected coupons in these washers by a factor of five — approximately the level of protection expected from a conversion of a type 317 stainless washer to a 6% Mo stainless steel.

Electrochemical protection of stainless vats is somewhat less effective, mainly because of corrosion of surfaces which are not immersed but are exposed to Cl₂ or ClO₂ vapors. Those areas exposed to the vapor above the pulp level are not protected by cathodic protection because they are not wetted by the electrolyte. In contrast to washer drums which are periodically rewetted (and reprotected) on each revolution, portions of stainless steel vats are never immersed in the pulp slurry. As a result, these areas are not electrochemically protected and may suffer from severe corrosion. Fortunately, corrosion above the liquid level is usually less of a concern since leakage is minimal.

Electrochemical protection may not extend to all internal drum components because of limitations on the "throwing power" of cathodic protection from a single anode. Drainage pipes, valves, flow channels, and other surfaces remote from the anode may not be protected, particularly if the shower water is high in Cl₂ or ClO₂. Protection of the outlet valve and/or drop leg discharge piping requires installation of a second system — complete with anodes and power supply — to achieve protection in this area. Although such installations have been made, they are rare because of the complexity of the system.

The cost of electrochemical protection arises from the capital installation, anodes installed in the vat, and electrical power. Overall, the typical installation to protect a washer drum is expected to cost less than one-fifth of the cost of a 316L replacement drum. Garner (14) has shown that electrochemical protection has a payback period of less than one year, assuming typical lifetimes of drum washers. The cost of electrical power and anode replacement has little effect on the calculation.

FRP Construction. A common method of controlling drum washer corrosion is the application of a glass-reinforced polyester or vinyl ester lining over a metal washer drum. In the typical installation, the FRP lining is a refurbishment of a drum that has corroded in prior bleach plant service. Extreme care is required to ensure adequate cleanliness of the refurbished drum prior to application of the FRP lining.

The lifetime of such FRP-lined equipment has generally been very good, although delamination of the lining and degradation of the polyester lining have occasionally been reported (15). Sharp (16) reported that more than 300 polyester FRP-lined units have been installed; some have had service lifetimes as long as twenty years without incident. Bardsley (11) claims that a five to ten year lifetime can be expected from the typical FRP-lining in bleach plant service.

FRP linings have also been widely used as vat linings and shower pipe linings, with considerable success.

The principal concern with FRP-lined washer drums is delamination or disbonding of the lining. Disbonding can occur because of differential thermal expansion between the metal drum and the polymeric lining material. Delamination also occurs because of stresses induced by differential thermal expansion, in this case in the resin-loaded lining itself. Limits may be placed on the rate of change of temperature of FRP-lined washers to minimize the danger of delamination.

Increased temperatures in chlorination stages have heightened concerns over disbonding and delamination. Higher stock temperatures increase the severity of thermal cycling that occurs with drum rotation. Higher temperatures also increase the permeability of resins, which can promote disbonding at the metal interface.

Monolithic FRP drums have been designed and installed to minimize concerns over disbonding during thermal cycling. These units are rare compared to lined washers. Since the modulus of FRP laminates is considerably lower than that of metals, care must be taken to provide adequate stiffeners for monolithic drums which are replacements for corroded stainless steel drums.

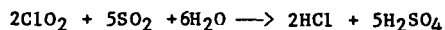
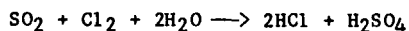
The type of resin used in FRP construction can have a significant effect on the durability of FRP linings in the bleach plant, but these differences should have relatively little effect on performance in washer applications. Significant differences might be anticipated in process equipment used in preparation of ClO_2 . Bergman (17) has shown that several of the Bisphenol-A polyesters and vinyl esters have good corrosion resistance in chlorine dioxide environments, including the following:

- * Bisphenol-A epoxy vinyl ester
- * Bisphenol-A fumarate polyester
- * HET-acid neopentyl glycol polyester

However, the resistance of a Bisphenol-A epoxy novolak vinyl ester was markedly superior to the above polyesters and vinyl esters, whereas a Bisphenol-A urethane vinyl ester was inferior.

Antichlor Compounds. The use of antichlor chemicals to quench residual chlorine or chlorine dioxide carryover into the washer stage is an effective method of reducing corrosion rates in bleach plant washers.

Two types of antichlor compounds are in general use. The first is SO_2 , which is added to the pulp between the C or D stage tower and the washer to react with and permanently destroy Cl_2 and ClO_2 . The reactions are:



The SO_2 reduces the residual oxidant con-

centration in the washer stage filtrates to zero, thereby reducing the aggressiveness of the environment. The acidification that accompanies antichlor reactions is not significant in terms of corrosion resistance. The second common antichlor is NaOH , which is used to neutralize acidic D-stage pulp between tower and washer. The alkalinity introduced significantly reduces the severity of attack of washer drums and related equipment.

The annual cost of using antichlor compounds is relatively high compared to the cost of a new washer drum. Garner estimates that the annual cost of either SO_2 or NaOH addition is on the order of one-fourth the cost of a type 316L replacement drum washer.

A third type of antichlor whose use is to be avoided is sodium thiosulfate, which is occasionally added to pulp following H stage washers to quench residual hypochlorite before papermaking. The residual thiosulfate introduced in this process is certainly more damaging than the hypochlorite, and the process is not recommended.

In summary, several methods have been identified which will reduce the damage associated with washers in C, D, and H stage service, but none of the current remedies is without cost. The approach for corrosion control in washers ranges from specification and periodic replacement of a marginal material of construction, to installation of a titanium drum for permanent resolution of corrosion concerns. More than one remedy may be used in any application to reduce overall costs.

CORROSION AND CONTROL IN CHEMICAL PREPARATION

The preparation, handling and storage of bleach plant liquors can be accomplished with limited corrosion damage, but careful attention must be paid to controlling process conditions and specification of resistant materials. Different precautions are required for each of the common bleaching agents, as summarized in the following paragraphs.

Chlorine Processing. The preparation of chlorine bleach liquors is relatively simple, consisting largely of evaporation of liquefied chlorine and metering the gaseous chlorine into the mixer preceding the bleaching tower.

Care must be taken to segregate wet and dry chlorine, since the corrosion resistance of materials of construction is usually very dependent on the presence of moisture. Catastrophic failure can occur if the moisture levels are inadvertently changed.

Dry chlorine in the liquid or gaseous state can be safely handled in plain carbon steel equipment, although uniform attack is rapid in wet chlorine gas. If carbon steel equipment is used, water content should be kept below 10 ppm by weight (18). Moisture can be introduced by failure to dry the padding air following compression, or by exposure of transfer equipment to the atmosphere during shutdown. Chlorine gas temperatures should be kept below 150 C. Laliberte (5) recommends seamless, Schedule 80, type A53 or A106 pipe.

Titanium must not be used in dry chlorine service or a pyrophoric reaction will rapidly destroy the metal. For example, Figure 5 shows a titanium heat exchanger used for wet chlorine evaporation which was destroyed by inadvertent exposure to dry chlorine. Chlorine gas must contain at least 0.3 percent water to prevent rapid pyrophoric attack of the titanium (12).

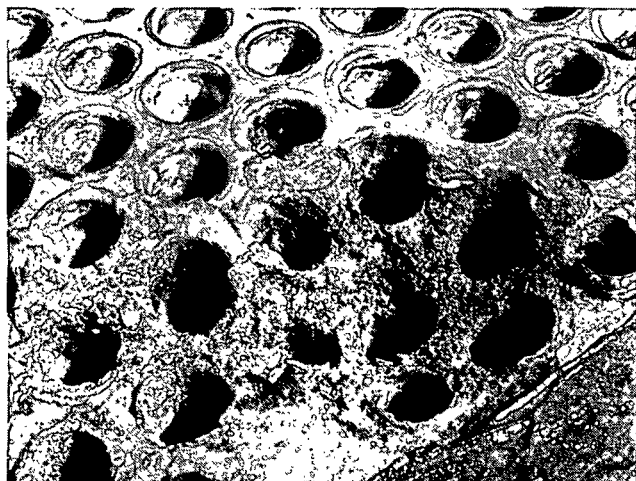


Fig. 5 Damage to a titanium heat exchanger exposed to dry chlorine gas, resulting in pyrophoric attack.

Wet chlorine can be safely handled in lead or titanium piping, or in steel piping lined with rubber, polyvinylidene chloride (Saran), polyvinylidene fluoride (PVDF), chlorinated polyvinyl chloride (CPVC), glass or lead. Different grades of titanium are available, and the less expensive Grade 2 is satisfactory in most exposures. To avoid crevice corrosion in very demanding applications, Grade 7 or Grade 12 titanium alloys should be used — for example, if the temperature of wet chlorine will exceed 200 F. The inlet to the chlorine mixer should be assumed to be a wet chlorine exposure.

The fluorocarbons and fluoroelastomers are generally resistant to both wet and dry chlorine to temperatures of 200 F. In particular, Viton A is appropriate for seals and gaskets in wet and dry chlorine gas and in liquid chlorine service.

Chlorine Dioxide. Since chlorine dioxide must be manufactured on site and all of the common generation processes are relatively complex, the selection of resistant materials and suitable process conditions is somewhat complicated. There are a number of processes used in the generation of chlorine dioxide. The common ClO_2 generation processes involve the reaction of sodium chlorate with SO_2 , methanol, or NaCl to produce ClO_2 in an acidic discharge containing some of the following: formic acid, residual methanol, Cl_2 , HCl and H_2SO_4 . Equipment required includes storage vessels for sodium chlorate and SO_2 (or sulfurous acid), hydrochloric acid, or methanol, one or more reaction vessels, an absorption tower (in some processes), storage for ClO_2 and spent brine, and miscellaneous piping.

Sodium chlorate solutions (20-40%) may be stored in steel tanks, but the lifetimes of such tanks are limited to only a few years. Type 304 stainless steel provides much better resistance at considerable additional expense. FRP tanks — vinyl ester with glass reinforcement and a thick resin liner — are widely used to store sodium chlorate solutions. Tile linings grouted with portland cement may also be used.

Methanol is usually stored in plain carbon steel tanks. It is noteworthy that titanium can experience stress corrosion cracking when exposed to methanol, and the use of titanium is contraindicated for this reason and for simple economics.

Dry sulfur dioxide may be stored and handled as a liquid or a gas in plain carbon steel equipment. Wet SO_2 (i.e., sulfurous acid) must be contained in stainless steel vessels (typically type 316L) or in lead or glass-lined vessels.

Concentrated sulfuric acid can be handled and stored in steel vessels, provided no moisture is present. A variety of thermosets and thermoplastic materials are resistant to dilute sulfuric acid but are attacked by concentrated sulfuric acid. In particular, the Bisphenol A polyester resin in an FRP construction is suitable for storage and handling of dilute sulfuric acid service (less than 70%) at temperatures below 180 F.

Generator vessels differ from mill to mill, depending on the mill experience and the exact ClO_2 generation process used. In the Solvay process, the reactor is typically lead-lined carbon steel. Reactors for the Mathieson process may be lead-lined or glass-lined steel, or steel vessels lined with acid brick, grouted with polyester resin, and isolated by a PVC membrane. Mathieson reactors may also be of FRP construction, with polyester and glass construction. Generators for the various R-processes are similar to those used in the Solvay and Mathieson processes.

Titanium has replaced some of the fiberglass generator vessels in recent years because of concerns over erosion of fiberglass in the inlet area. Titanium inserts are also being used to shield existing FRP vessels from erosion.

Occasional instances of crevice corrosion of titanium tubes in ClO_2 reboilers have been reported. An example of this titanium corrosion is shown in Fig. 6. Care must be taken to ensure that the temperature remains below 200 F if Ti Grade 2 is in contact with wet chlorine. If higher temperatures are likely, Ti Grade 7 or Ti Grade 12 should be used.

The typical ClO_2 storage tank is a filament-wound FRP vessel utilizing glass reinforcement and either vinyl ester or polyester resin. Steel vessels lined with acid brickwork are also used, provided an appropriate membrane is incorporated between the brickwork and the shell. Depending on temperature, ClO_2 lines are typically PVC, Saran, or PVDF with Hastelloy C or titanium trim.

Peroxide. Peroxide bleach liquors are usually prepared on site from sodium and hydrogen perox-

ides, sodium hydroxide, sodium silicate, and magnesium sulfate. Peroxide may also be added directly to alkaline extraction stages or added to pulp in high density storage to raise brightness and reduce brightness reversion.

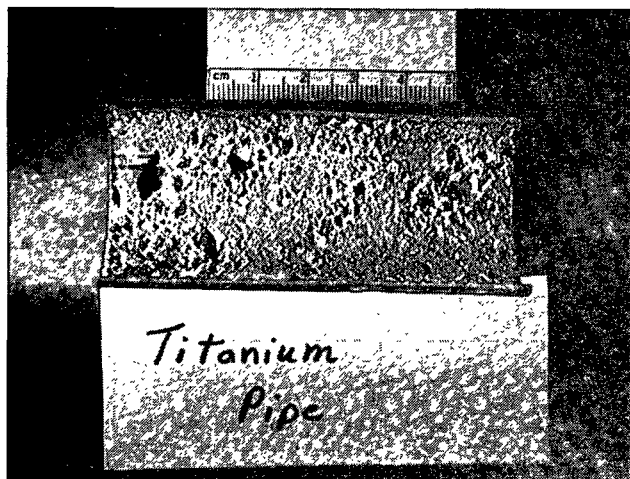


Fig. 6 Crevice corrosion of a Ti Grade 2 tube in a chlorine dioxide reboiler.

Dilute solutions of sodium hydroxide and sodium silicate are usually stored and handled in plain carbon steel equipment with stainless steel valves and trim. Maintaining sodium hydroxide concentrations below 50% and temperatures below 120 F will prevent stress corrosion cracking (i.e., caustic cracking) of carbon steel at welds and other locations where stresses are present.

Pure hydrogen peroxide is usually stored in aluminum vessels, whereas the more alkaline sodium peroxide is usually stored and handled in either type 316L or 317L stainless steel vessels. In general, titanium is not suitable for use with peroxides, since reactions with alkaline peroxides can be very rapid (12). Once prepared, the peroxide bleach liquors can be stored in 316L or 317L stainless steel vessels, as well.

CONTROLLING ATMOSPHERIC CORROSION IN THE BLEACH PLANT

Bleach plant equipment is seldom gas-tight, and most bleach plants are steadily or periodically bathed in gases or liquids inadvertently discharged from the bleaching equipment. The rate of attack on unprotected structural steel and concrete can be very rapid unless protective measures are adopted — usually the application of corrosion-resistant coatings. Atmospheric corrosion of electronic equipment can also be severe unless steps are taken to isolate electronic and electrical hardware from contact with the bleach plant atmosphere (19).

Corrosion of Structures

Precautions must be taken to prevent premature failure of structural steel in bleach plant applications. Plain carbon steel is used widely for structural supports, building walls and roofing,

walkways and grating, auxiliary piping, and related components. Plain carbon steel is usually protected by a coating applied to the surface, and this is particularly important in the bleach plant where spills and vapor discharges produce severe environments.

The Steel Structures Painting Council recommends that steel structures in the bleach plant be coated with a zinc-rich inorganic primer followed by two or more coats of a chemical-resistant, high-build topcoat material (20). Where the attack is moderate, the recommended topcoat is a high-build amine-cured epoxy or polyurethane coating. For zones where frequent spills occur, or where the exposure approaches immersion service, vinyl topcoats are recommended and generally give good service if properly applied.

Precautions should also be taken to minimize the retention of water on coated steel surfaces in the bleach plant, since few coatings will be resistant if continually wetted. Roof sections should be insulated against condensation of moisture and kept in good repair to prevent rainwater from entering. Good ventilation is also important for prevention of condensation, as well as removal of corrosive gases. For the same reason, careful sealing of bleach plant equipment and avoidance of spills and poor housekeeping can reduce corrosion of structural supports. Adequate drainage is important to prevent pooling of water and the severe coating damage that can result.

Concrete is another structural material that can suffer from atmospheric exposure in the bleach plant. Although concrete is typically quite resistant to alkaline environments, it suffers from rapid attack in acidic environments. Spillage of C or D stage filtrates on concrete will result in very rapid deterioration. Acids associated with chemical generation can be equally aggressive.

Spallation can also be a concern where moisture and salts penetrate reinforced concrete structures. The corrosion products formed on the reinforcing bar expand and spall the concrete, thereby exposing the rebar to further corrosion and accelerating the rate of damage. This is a particular concern in the bleach plant, since chlorides are everywhere.

Concrete can be protected from attack in a variety of ways. Concrete placed with a high cement:water composition is much less permeable than the common concrete grades and is more resistant to spallation by reinforcing bar corrosion. Rebar corrosion can also be prevented by using epoxy-coated reinforcing bars in the original construction. Polymer concrete has been used to increase the resistance of concrete to prevent concrete degradation in bleach plant environments. Latex or epoxy may be added to portland cement concrete formulations to increase corrosion resistance. Polymer concrete may also be used, with the portland cement replaced as the binder by polymeric resins. Finally, sulfur concrete in which hot melt sulfur is the binder can be used to improve concrete corrosion resistance.

Concrete can also be protected by application

of a coating to the concrete surface, although some care is required to ensure adhesion. Concrete floors and motor pedestals can be coated with vinyl to improve corrosion resistance. Successful coating requires that the surface be adequately prepared in terms of cleanliness and profile. If new concrete is to be coated, petroleum-based form release compounds should not be used, since they interfere with coating adhesion. Ideally, concrete should be cured for thirty days without exposure to the elements before the surface is coated. Since this is often impractical, especially with repair patches, the concrete should either be acid-etched and thoroughly washed, or be given a dust blast to remove surface contaminants.

Polymer concrete formulations are often a better alternative than coated concrete for repair projects.

For harsh service, concrete can be protected by the installation of either FRP linings or tile and grout linings identical to those used in towers, vats, etc. Ceramic tile set in polyester sand mortar is appropriate for most applications (excepting hypochlorite service where portland cement is used in place of polyester). Alternatively, FRP linings with glass roving set in place with polyester or vinyl ester resins and a heavy resin topcoat may be used. These methods are commonly used to protect floors and pedestals subjected to frequent spillage.

Electronic Equipment

The chlorinated gases emanating from the bleach plant can be very damaging to delicate electronic components used in modern process control equipment. Silver contacts, terminals, and wire wraps are particularly susceptible to chlorine damage, even at contaminant levels approaching the parts per billion level (21).

The practical alternative for protecting electronic equipment is encapsulation of sensing components and purification of the air surrounding central electronics and computer control equipment. Encapsulation usually involves potting electronics in hermetically sealed or gasketed enclosures. A cost involved in encapsulation is inaccessibility for repair. Air purification usually involves isolation procedures to prevent ingress of corrosive gases, humidity control and, in severe cases, installation of gas cleaning equipment.

SUMMARY

The environments found in the typical bleach plant are highly corrosive, and care must be taken to minimize costs associated with corrosion and corrosion-induced loss of production. In most cases, materials have been identified which are fully resistant to attack in each of the environments associated with bleaching. Use of these resistant materials may or may not be the optimal method of corrosion control, since other options, such as electrochemical protection and modification of the environment, may be more cost effective. Fortunately, the choice of corrosion control options can be tailored to match the corrosion control strategy of the mill. Such strategies may

range from periodic replacement of marginal materials to routine specification of exotic and expensive materials of construction.

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